



IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Application No. : 10/820,135 Confirmation No.: 6664
Applicant : Nils KJELLBERG, et al.
Filed : April 8, 2004
TC/A.U. : 1711
Examiner : To Be Assigned
Docket No. : 038724.53972US
Customer No. : 23911
Title : Brine Separation in Tall Soap Oil Preparation

CLAIM OF PRIORITY UNDER 35 U.S.C. § 119

Mail Stop Missing Parts
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

The benefit of the filing date of prior foreign application No. 01124064.5, filed in Europe on October 9, 2001, is hereby requested and the right of priority under 35 U.S.C. § 119 is hereby claimed.

In support of this claim, filed herewith is a certified copy of the original foreign application.

Respectfully submitted,

August 23, 2004

Vincent J. Sunderdick
For Donald D. Evenson
Registration No. 26,160
VINCENT J. SUNDERDICK
Registration No. 29,004

CROWELL & MORING LLP
Intellectual Property Group
P.O. Box 14300
Washington, DC 20044-4300
Telephone No.: (202) 624-2500
Facsimile No.: (202) 628-8844
DDE:ms #334424

BEST AVAILABLE COPY

THIS PAGE BLANK (USPTO)



Europäisches
Patentamt

European
Patent Office

Office européen
des brevets

Bescheinigung

Certificate

Attestation

Die angehefteten Unterlagen stimmen mit der ursprünglich eingereichten Fassung der auf dem nächsten Blatt bezeichneten europäischen Patentanmeldung überein.

The attached documents are exact copies of the European patent application described on the following page, as originally filed.

Les documents fixés à cette attestation sont conformes à la version initialement déposée de la demande de brevet européen spécifiée à la page suivante.

Patentanmeldung Nr. Patent application No. Demande de brevet n°

01124064.5

Der Präsident des Europäischen Patentamts:
Im Auftrag

For the President of the European Patent Office

Le Président de l'Office européen des brevets
p.o.

R C van Dijk

**CERTIFIED COPY OF
PRIORITY DOCUMENT**

THIS PAGE BLANK (USPTO)



Anmeldung Nr:
Application no.: 01124064.5
Demande no:

Anmeldetag:
Date of filing: 09.10.01
Date de dépôt:

Anmelder/Applicant(s)/Demandeur(s):

Linde AG
Abraham-Lincoln-Strasse 21
65189 Wiesbaden
ALLEMAGNE

Bezeichnung der Erfindung/Title of the invention/Titre de l'invention:
(Falls die Bezeichnung der Erfindung nicht angegeben ist, siehe Beschreibung.
If no title is shown please refer to the description.
Si aucun titre n'est indiqué se referer à la description.)

Brine separation in tall soap oil preparation

In Anspruch genommene Priorität(en) / Priority(ies) claimed /Priorité(s)
revendiquée(s)
Staat/Tag/Aktenzeichen/State/Date/File no./Pays/Date/Numéro de dépôt:

Internationale Patentklassifikation/International Patent Classification/
Classification internationale des brevets:

D21C11/00

Am Anmeldetag benannte Vertragsstaaten/Contracting states designated at date of
filing/Etats contractants désignées lors du dépôt:

AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU MC NL PT SE TR

The applicant's name at the time of filing of the application was as follows:
Linde Gas AG - Höllriegelskreuth, Germany

The registration of the change has taken affect on 12 December 2001 (12.12.2001)

THIS PAGE BLANK (USPTO)

Specification

Brine Separation in Soap Oil Preparation

The present invention relates to a process for improving the separation of aqueous sodium bicarbonate brine from soap oil in the recovery process of a pulp mill,
5 comprising: forming a mixture comprising crude tall oil soap, water and carbon dioxide, neutralising the crude tall oil soap and separating the aqueous sodium bicarbonate brine and the soap oil obtained from said neutralisation step.

The invention is further related to a process for improving the separation of aqueous sulphate brine from crude tall oil in the recovery process of a pulp mill, comprising:
10 forming a mixture comprising soap oil, water and sulphuric acid, acidulating said soap oil and separating the aqueous sulphate brine and the crude tall oil obtained from said acidulation step.

15 In chemical pulping wood chips are cooked with appropriate chemicals in an aqueous solution to obtain a fibrous mass. In this process the spent cooking liquor containing several chemicals is recycled. In the following the recycling of the cooking liquor will be referred to as recovery process or recovery system. The recovery process essentially comprises the separation of crude tall oil soap from black liquor, the crude tall oil
20 preparation process, the evaporation of black liquor and subsequently its burning in the recovery boiler, the alkalisation of green liquor received from the recovery boiler and its recycling to the cooking process step.

The cooking liquor is separated from the fibres and washed with water forming weak
25 black liquor. Reacted resin acids and fatty acids which rise to the surface of the black liquor are skimmed off as crude tall oil soap. The black liquor may be subjected to one or more evaporation stages to form strong black liquor with increased solid contents. Additional crude tall oil soap may be removed at these stages.

30 The strong black liquor is introduced into the recovery boiler which evaporates residual moisture from the liquor, burns the organic constituents and supplies heat for steam generation. The flue gases from the recovery boiler containing a lot of chemicals are passed through an electrostatic precipitator to separate the recovery boiler ash. The

recovery boiler ash is a salt mixture essentially containing sodium sulphate and sodium carbonate. Normally the ash is directly recycled into the recovery system by dissolving the ash in the black liquor that is going to be burnt in the recovery boiler.

- 5 The crude tall oil soap skimmed off the liquor is traditionally acidulated with sulphuric acid to a pH of about 3 or lower. At this reaction three phases are formed: crude tall oil, a mixed phase containing fiber and lignin residuals and a aqueous sulphate brine solution. The brine solution and the mixed phase are separated and returned to the recovery system. Sometimes this mixed phase causes problems as it sticks to the equipment and extra cleaning is necessary. The obtained crude tall oil is used internally as a fuel or externally as a valuable raw material for the chemical industry.

- 15 The consumption of sulphuric acid in the acidulation of the crude tall oil represents an increasing problem to modern pulp mills. The amount of sulphuric acid for this reaction forms a major part of the total intake of sulphur make-up to the recovery system of the pulp mill. However, due to environmental considerations sulphur emissions into the environment are increasingly unacceptable and there is a strong need to reduce the amount of sulphur and sulphuric compounds required in the recovery process of a pulp mill.

- 20 The sulphuric acid consumption may be reduced by about 30% to 50% by a pre-treatment of the crude tall oil soap with carbon dioxide. According to such a process which is disclosed in WO 98/29524 the crude tall oil soap is subjected to carbonic acid prior to the final separation of black liquor and soap whereby cleaning the crude soap from impurities and hence reducing the amount of acid to acidify the soap. The carbon dioxide acidulation has the further advantage that the sticky components of the mixed phase are dissolved in the sodium bicarbonate brine and do not stick to the equipment.

- 30 In the technical operation it is difficult to obtain a high degree of bicarbonate brine separation from the soap oil after the carbon dioxide neutralisation step due to the creamy consistency of the soap oil. However, remaining bicarbonate brine in the soap oil will increase the sulphuric acid consumption in the final acidification step which for environmental reasons is to be avoided.

To overcome this problem WO 96/34932 suggests to carry out an additional step of pH adjustment after the carbon dioxide pre-treatment but prior to the bicarbonate brine separation step. The pH adjustment may be performed by an acidically reacting substance, such as sulphuric acid or bisulphite. One drawback of this solution is that it is also reducing the efficiency of the carbon dioxide pre-treatment as it will increase the amount of sulphur introduced into the recovery system.

An object of the present invention is to provide an improvement in the separation of bicarbonate brine in the soap oil preparation process and to reduce the amount of sulphuric compounds required in the final acidulation step.

Another object of the present invention is to improve the separation of sulphate brine and crude tall oil in the final acidulation of the crude tall oil preparation process.

The characteristics of the present invention are defined in the appended claims.

Consequently, the invention relates to a process for improving the separation of sodium bicarbonate brine from soap oil in a tall oil recovery process comprising the following steps: The crude tall oil soap is mixed with a special high-density water solution and carbon dioxide. The resulting acid neutralises the crude tall oil soap whereby forming a two phase solution of crude soap oil and sodium bicarbonate brine. Subsequently the aqueous sodium bicarbonate brine is separated from the soap oil obtained.

After the separation of the sodium bicarbonate brine from the soap oil a final acidulation is carried out. After the final acidification it can also be difficult to get a good separation of the resulting sulphate brine from the resulting crude tall oil. This is due to the reduced difference in density between the phases which is a consequence of the reduced charge of sulphuric acid in the final acidulation step.

It has been found that the use of the inventive high density water solution is also advantageous in the final acidulation step as an additive to the sulphuric acid. This will result in sulphate brine with higher density that thus is easier to separate from the crude tall oil phase. The water and brine content of the final crude tall oil is minimised, increasing the quality and the effective yield of crude tall oil.

According to one embodiment carbon dioxide is first dissolved in said water solution having increased density to form an acidic solution and afterwards the crude tall oil soap is neutralized with said acidic solution.

- 5 It is also advantageous to first dilute the crude tall oil soap with said water solution having increased density and then introduce carbon dioxide into the soap-water solution.

- 10 Due to the inventive use of water having an increased density the carbon dioxide treatment results in a bicarbonate brine with higher density compared to the state of the art processes. Thus it is easier to separate the soap oil and the brine solution.

- 15 The high density water is preferably prepared by mixing ash and / or dust from the recovery process, in particular precipitator ash, with water. Beside the desired increase in the density of the water such a preparation has the additional advantage that no other substances, in particular no additional chemicals, are added to the recovery process.

- 20 Ash and dust are separated by an electrostatic precipitator from the flue gases of the recovery boiler. Normally that precipitator ash or dust is recirculated to the recovery system by mixing it to the strong black liquor prior to entering the recovery boiler. According to the invention the precipitator ash is not directly recirculated to the black liquor, but first used to form said high-density water. The high-density water is mixed with the crude tall oil soap and carbon dioxide for the soap neutralisation or, in the
25 acidulation step, is mixed with soap oil and sulphuric acid. In this way the precipitator ash is also returned to the black liquor and the recovery boiler, however the recovery cycle is longer. Compared to the known processes the precipitator ash is additionally used to form said high density water solution before ending up in the same position, that is in the black liquor system. According to the invention no additional external
30 sulphate is added to the recovery process.

- The invention uses the physical effects due to the difference in density between the soap oil respectively the tall oil and the brine phases when using the high-density water solution. However, a too high density may limit the carbon dioxide solubility in the water
35 which reduces the achievable pH in the soap treatment. This is disadvantageous as a

pH of about 8 should be reached in order to have the separation of soap oil and bicarbonate brine. Therefore, an increasing density of the water solution has the positive effect of increasing the relative density difference between the bicarbonate brine and the soap oil, but the negative effect of decreasing the soap oil formation. It
5 has been found that the optimum water solution should have a density between 1000 kg/m³ and 1500 kg/m³, preferably between 1050 kg/m³ and 1300 kg/m³ and most preferably between 1100 kg/m³ and 1200 kg/m³.

10 In a preferred embodiment sodium and/or potassium salts of sulphate and/or carbonate and/or chloride are used to increase the density of the water. Such salts may be sodium sulphate, sodium carbonate, sodium chloride or mixtures thereof. Preferably ash or dust from the recovery boiler is dissolved in the water that is used to dissolve carbon dioxide therein.

15 The water, that is prepared in the inventive manner, could be fresh water or, preferred, water or an aqueous solution recirculated within the recovery process. It is for example possible to use a partially recycled sulphate brine solution, another internally recirculated liquid as e.g. an evaporation condensate or anything similar.

20 After the separation of the sodium bicarbonate brine from the soap oil the final acidulation is preferably carried out with sulphuric acid or spent acid from the chlorine dioxide preparation. The spent acid, a waste stream from the pulp mill, is a mixture of sulphuric acid and sodium sulphate. The amount of sulphuric acid or spent acid necessary is reduced by about 30% to 50% compared to processes without carbon
25 dioxide pre-treatment. As a result of the acidulation a sulphate brine phase and a crude tall oil phase are formed.

Preferably the change in pH after the neutralisation of the crude tall oil soap and prior to the separation of sodium bicarbonate from soap oil is less than 0.2, more preferred
30 less than 0.1, and most preferred there is essentially no change in pH. According to a preferred embodiment of the present invention the neutralisation step is directly followed by the separation of the bicarbonate brine without any intermediate addition of any substances, in particular without adding any pH changing substances.

Using the recovery boiler ash in the proposed manner the external intake of sulphur to the pulp mill recovery system is not influenced and thus the full efficiency of the carbon dioxide pre-treatment to reduce the mill sulphur intake will be maintained or even improved as less remaining bicarbonate brine in the soap oil will further reduce the sulphuric acid needed in the final acidulation.

The invention will now be illustrated in greater detail with reference to the appended drawings. It is obvious for the man skilled in the art that the invention may be modified in many ways and that the invention is not limited to the specific embodiment described in the following example.

In

- | | |
|----------|---|
| figure 1 | a schematic drawing of the tall oil recovery system is shown, |
| figure 2 | shows the same system with a different order of mixing and |
| figure 3 | shows another embodiment of the inventive system. |

As schematically shown in figure 1 water 1 and recovery boiler ash 2 are introduced into a dissolving tank 3. The recovery boiler ash is a mixture of about 90% sodium sulphate, 9% sodium carbonate and 1% sodium chloride and is separated from the recovery boiler flue gases by using electrostatic precipitators. In the dissolving tank 3 a special water solution 15 is prepared which has an increased density of 1200 kg/m^3 achieved by dissolving ash and dust 2 from the recovery boiler into the water 1.

The high density water solution 15 is fed to a vessel 4. Further carbon dioxide gas 5 is introduced into the vessel 4 and dissolved in the high density water solution 15. The so prepared high density carbonic acid solution is pumped to the tall oil plant. In the tall oil plant crude tall oil soap 6 is neutralized with the high density water solution in a neutralisation reactor 7.

After this carbon dioxide pre-treatment process two phases are formed within the neutralisation reactor 7, a bicarbonate brine which collects at the bottom of the neutralisation reactor 7 and the soap oil phase on top of the brine. Due to the inventive use of the special high density water 15 the bicarbonate brine has an increased density compared to brine resulting from the state of the art neutralisation reactions. Thus the

brine can easily be separated from the soap oil and is returned to the recovery process 8.

5 The soap oil phase is fed from the neutralisation reactor 7 via pipe 9 to the acidulation reactor 10. In the reactor 10 the soap oil is finally acidulated with sulphuric acid 11 and an additive of the high density water solution 15. After the acidulation a sulphate brine phase and a crude tall oil phase are obtained. As a consequence of the addition of the high density water solution 15 the sulphate brine has an increased density and is thus easier to separate from the crude tall oil phase. The tall oil 12 is gathered from the top 10 of the acidulation reactor 10 whereas the sulphate brine 13 is recycled in the recovery process.

15 Instead of first introducing carbon dioxide 5 into the high density water solution 15 and then mixing the resulting carbonic acid with crude tall oil soap 6, it is also advantageous to change the order of adding carbon dioxide 5 and crude tall oil soap 6. Such a process is shown in figure 2. First crude tall oil soap 6 is diluted with the high-density water 15 obtained from vessel 3. Into the resulting solution carbon dioxide 5 is introduced to neutralize the crude tall oil soap 6.

20 The above described process may also be performed as a continuous process, that is instead of using separate reactors 3, 4, 7, 10, some or all of these process steps can be done in one reactor vessel. One such example is shown in figure 3. Instead of using two vessels 4, 7, as shown in figures 1 and 2, the high density water 15, carbon dioxide 5 and crude tall oil soap 6 are mixed in one vessel 14. It is also possible to have only 25 one vessel instead of vessels 3 and 14 or to have one common reactor vessel for all described process steps.

THIS PAGE BLANK (USPTO)

EPO - Munich
6
09. Okt. 2001

Claims

1. A process for improving the separation of aqueous sodium bicarbonate brine from soap oil in the recovery process of a pulp mill, comprising:
forming a mixture comprising crude tall oil soap, water and carbon dioxide,
5 neutralising the crude tall oil soap and
separating the aqueous sodium bicarbonate brine and the soap oil obtained from said neutralisation step,
characterized in that
said mixture comprises a water solution (15) having an increased density.
10
2. A process for improving the separation of aqueous sulphate brine from crude tall oil in the recovery process of a pulp mill, comprising:
forming a mixture comprising soap oil, water and sulphuric acid,
acidulating said soap oil and
15 separating the aqueous sulphate brine and the crude tall oil obtained from said acidulation step,
characterized in that
said mixture comprises a water solution (15) having an increased density.
- 20 3. A process according to claim 1 characterized in that said crude tall oil soap (6) is diluted with said water solution (15) having increased density and then mixed with carbon dioxide (5).
- 25 4. A process according to any of claims 1 to 3 characterized in that ash and / or dust (2) from the recovery process, in particular precipitator ash, is mixed with water (1) to form said water solution (15) having an increased density.
- 30 5. A process according to claim 4 characterized in that sodium and / or potassium salts of sulphate and / or carbonate and / or chloride are dissolved in said water (1) to form said water solution (15) having an increased density.
6. A process according to any of claims 1 to 5 characterized in that said water solution (15) has a density between 1000 kg/m^3 and 1500 kg/m^3 , preferably

between 1050 kg/m³ and 1300 kg/m³, most preferably between 1100 kg/m³ and 1200 kg/m³.

- 5 7. A process according to any of claims 4 to 6 characterized in that said water solution (15) having increased density is prepared by mixing said ash and / or dust (2) with water (1) recirculated within the recovery process.
- 10 8. A process according to claim 7 characterized in that said ash and / or dust (2) is mixed with water (1) containing sulphate brine solution.
- 15 9. A process according to any of claims 1 to 8 characterized in that said soap oil (9) is treated with sulphuric acid (11).
- 20 10. A process according to claim 9 characterized in that said water solution (15) having an increased density is added to said sulphuric acid (11).
11. A process according to any of claims 1 to 10 characterized in that after said neutralisation step and prior to said separation step of said sodium bicarbonate brine and said soap oil the change in pH is less than 0.2, preferably less than 0.1, and most preferably there is no change in pH.

09. Okt. 2001

Abstract

Brine Separation in Soap Oil Preparation

5 The invention is directed to a process for improving the separation of sodium bicarbonate brine from soap oil or of sulphate brine from crude tall oil in the recovery process of a pulp mill. In the neutralisation/acidulation of crude tall oil soap (6) or soap oil (9) with carbon dioxide (5) respectively sulphuric acid (11) a water solution (15) having an increased density is used. (figure 1)

THIS PAGE BLANK (USPTO)

Fig. 1

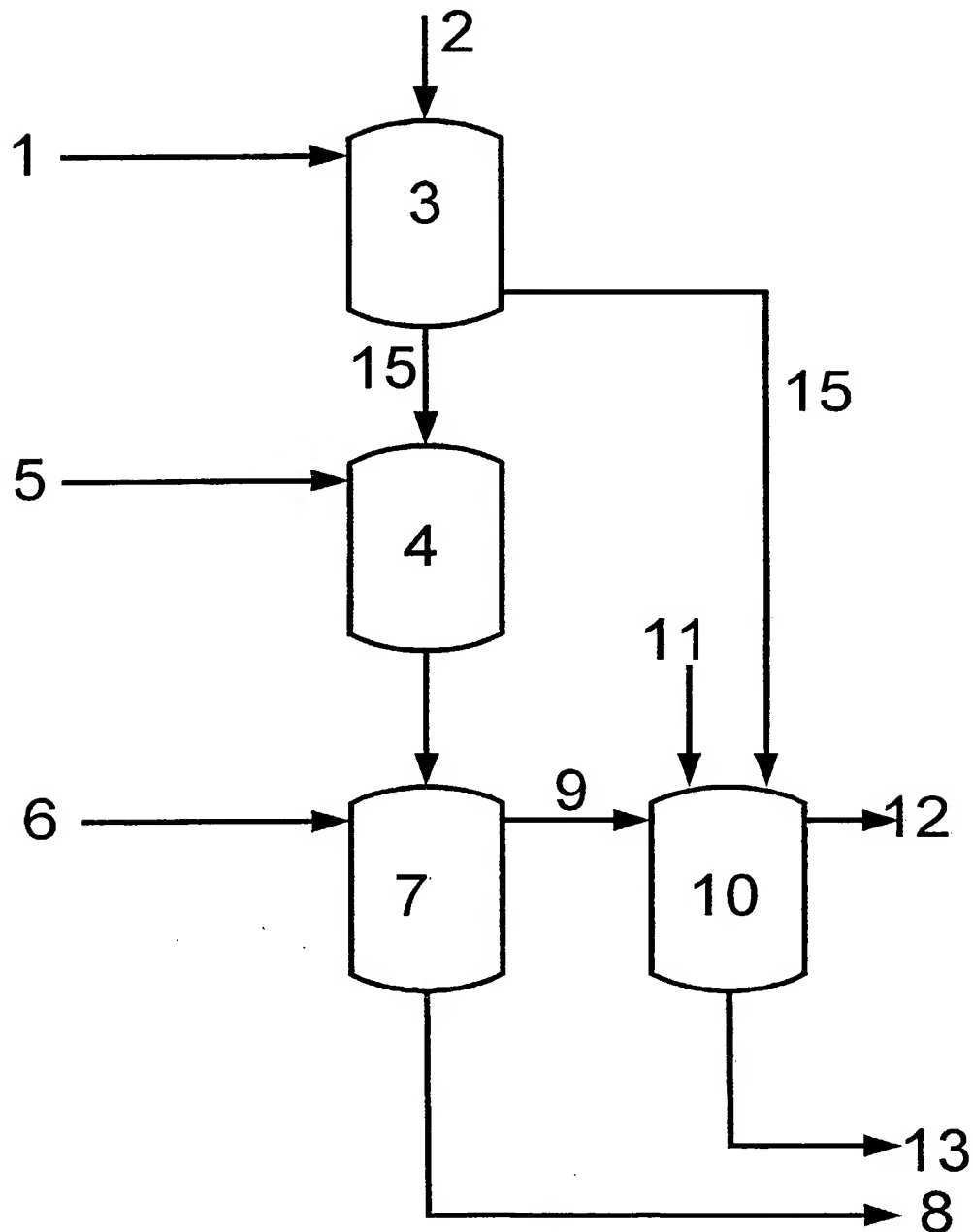


Fig. 2

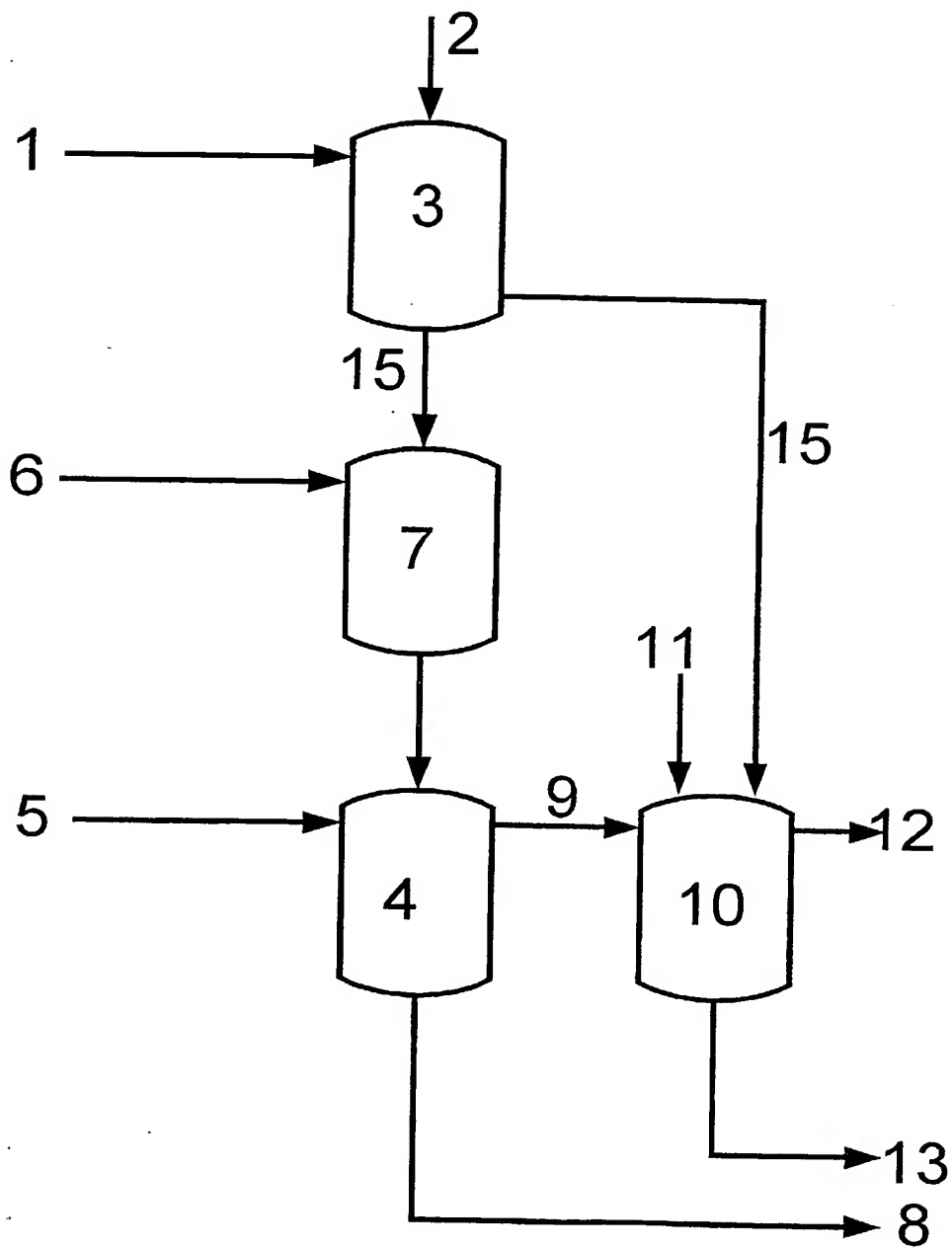
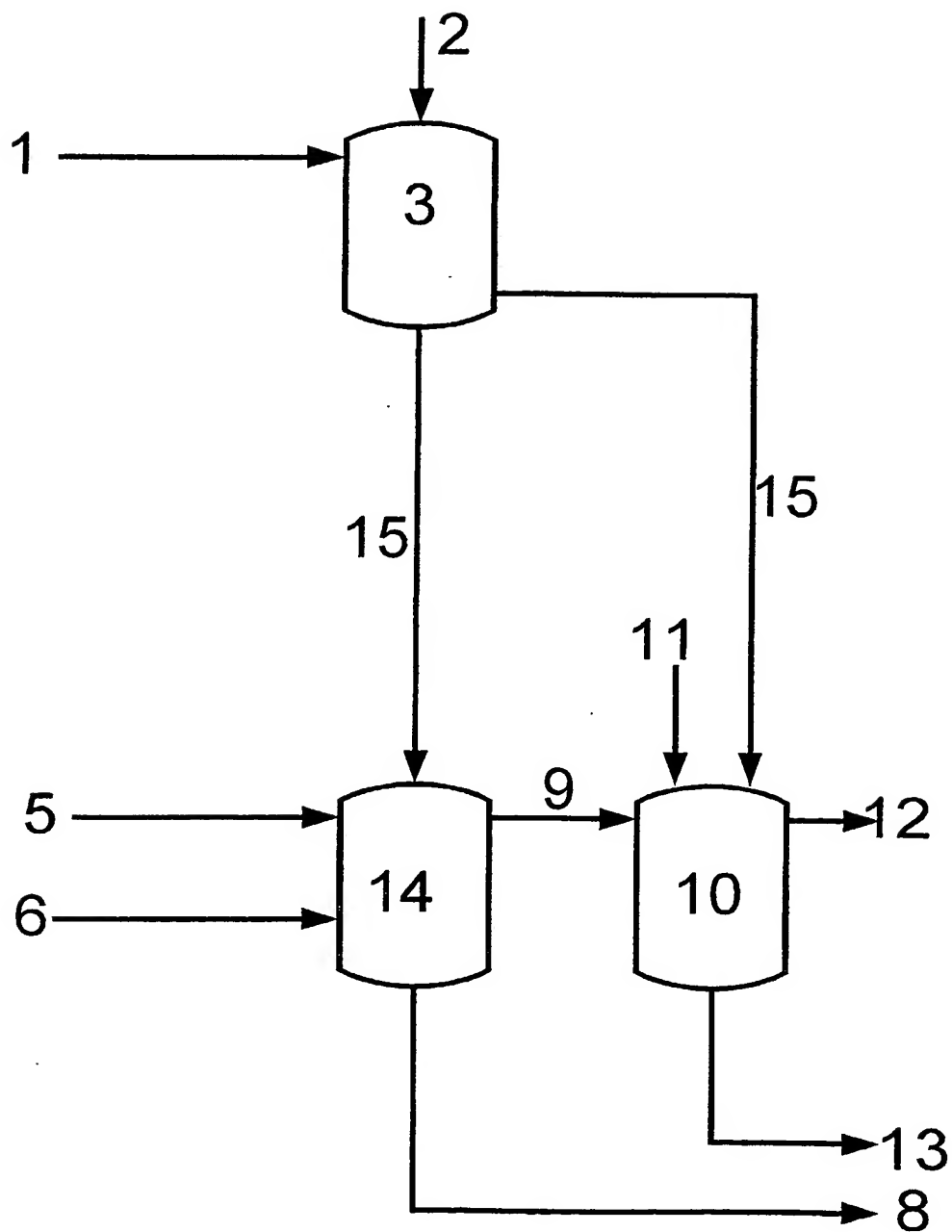


Fig. 3



THIS PAGE BLANK (USPTO)

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☒ **BLACK BORDERS**
- ☐ **IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**
- ☐ **FADED TEXT OR DRAWING**
- ☐ **BLURRED OR ILLEGIBLE TEXT OR DRAWING**
- ☐ **SKEWED/SLANTED IMAGES**
- ☐ **COLOR OR BLACK AND WHITE PHOTOGRAPHS**
- ☐ **GRAY SCALE DOCUMENTS**
- ☐ **LINES OR MARKS ON ORIGINAL DOCUMENT**
- ☐ **REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**
- ☐ **OTHER:** _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.

THIS PAGE BLANK (USPTO)